Synopsis

The aim of the present thesis is to understand the phase transformation behavior of embedded alloy nanoparticles embedded in immiscible matrices. Embedded alloy inclusions have been dispersed in immiscible matrix via rapid solidification method. The present work deals with synthesis of embedded particles, evolution of microstructure, morphology and crystallographic orientation relation relationships among different phases, phase transformation and phase stability behavior of embedded alloy inclusions in different matrices. In the present investigation the systems chosen are Bi-Sn and Bi-Pb in Zn matrix and Cd-Sn in Al matrix.

Chapter 1 gives the brief introduction of present work

Chapter 2 gives a brief review of nanoscale materials, various synthesis techniques, microstructure evolution, solidification and melting theories.

Chapter 3 discusses the processing and experimental techniques used for characterization of the different samples in the present work. Melt-spinning technique used to synthesize the rapidly solidified ribbons. The structural characterization is carried out using X-ray diffraction and transmission electron miscoscopy.

Chapter 4 illustrates the size dependent solubility and phase transformation behavior of Sn-Cd alloy nanoparticles embedded in aluminum matrix. X-ray diffraction study shows the presence of fcc Al, bct Sn, hcp Cd solid solution and hcp Cd phases. Based on Zen's law, the amount of Sn present Cd solid solution is estimated. Using overlapped sterograms, the orientational relationships among various phases are found. Microscopy studies reveal that majority of the alloy nano inclusions exhibit a cuboctahedral shape with 111 and 100 facets and they are bicrystalline. STEM-EDS analysis shows that both phases exhibit size dependent solubility behavior and for particles size smaller than 18 nm, single phase solid solution could only be observed. Calorimetric studies reveal a depression in eutectic melting point of bimetallic particles. *In situ* heating studies show that melting initiates at triple line junction corner and melt first grows into the interior of the Sn rich phase of the particle and then later the melt grows into the interior of the Cd phase of the particle. During cooling first Cd phase solidifies later Sn phase solidifies and on further cooling at low temperatures entire particle transforming into complete solid solution phase particle. Size dependent melting studies show that during heating smaller particles melted first, later bigger particles melted. During cooling first bigger particle solidified later smaller particles solidified. High resolution imaging indicates presence of steps across particle-matrix interface that may get annihilated during heating. During cooling, molten particles in the size range of 16-30 nm solidify as solid solution which for molten particles greater than 30 nm solidify as biphasic particle. *Insitu* heating studies indicates that for solid particles less than 15 nm get dissolved in the Al matrix at temperatures at around 135°C. Differential scanning calorimetry (DSC) studies show in the first heating cycle most of the particles melt with an onset of melting of at 166.8°C which is close to the bulk eutectic temperature of Sn-Cd alooy. The heating cycle reveals that the melting event is not sharp which can be understood from in-situ microscopy heating studies. In the second and the third cycles, the onset of melting observed at still lower temperatures 164.3°C and 158.5°C .The decrease in onset melting point in subsequent heating cycles is attributed to solidsolution formation of all small particles whose size range below 30 nm during cooling. cooling cycles exhibit an undercooling of 90°C with respect to Cd liquidus temperature. Thermal cycling experiments using DSC were carried out by arresting the run at certain pre-determined temperatures during cooling and reheating the sample to observe the change in the melting peak position and area under the peak. The areas of these endothermic peaks give us an estimate of the fraction of the particles solidified upto the temperature when the cycling is reversed. Based on experimental observations, a thermodynamic model is developed, to understand the solubility behavior and to describe the eutectic melting transition of a binary Sn-Cd alloy particle embedded in Al matrix.

Chapter 5 discusses the phase stability and phase transformation behavior of nanoscaled Bi-Sn alloys in Zn matrix. Bi-Sn alloys with eutectic composition embedded in Zn matrix using melt spinning technique. X-ray diffraction study shows the presence of rhombohedral Bi, pure BCT Sn and hcp Zn phases. In X-ray diffractogram, there are also other new peaks observed, whose peak positions (interplanar spacings) do not coincide either with rhombohedral Bi or bct Sn or hcp Zn. Assuming these new phase peaks belong to bct Sn rich solid solution(based on earlier work on Bi-Sn rapidly solidified metastable alloys) whole pattern fitting done on x-ray diffractogram using Lebail method. The new phase peaks indicated as bct M1(metastable phase1), bct M2(metastable phase2) phases. The amount of Bi present in M1, M2 solid solution is estimated using Zens law. Two sets of inclusions were found, one contains equilibrium bismuth and tin phases and the other set contains equilibrium bismuth and a metastable phase. In-situ TEM experiments suggest that as temperature increases bismuth diffuses into tin and becomes complete solid solution. Melting intiates along the matrix–particle interface leading to a core shell microstructure. During cooling the entire inclusion solidify as solid solution and decomposes at lower temperatures. High temperature XRD studies show that as temperature increases M1, M2 phases peaks merge with Sn phase peaks and Bi phase peak intensities slowly disappear and on further increasing temperature Sn solid solution phase peaks also disappear. During cooling diffraction studies show that first Sn solid solution phase peaks appear and later Bi phase peaks appear. But, the peaks belong to metstable phases not appeared while cooling.

Chapter 6 presents morphology and phase transformation of nanoscaled bismuth-lead alloys with eutectic ($Pb_{44.5}$-$Bi_{55.5}$) and peritectic (Pb_{70}-Bi_{30}) compositions embedded in zinc matrix. using melt spinning technique. In alloy1[Zn-2at%($Pb_{44.5}$-$Bi_{55.5}$)] inclusions were found to be phase separated into two parts one is rhombohedral Bi and the other is hcp Pb_7Bi_3 phase. X-ray diffraction study shows the presence of rhombohedral Bi, hcp Pb_7Bi_3 and hcp Zn phases in Zn-2at%($Pb_{44.5}$-$Bi_{55.5}$) melt spun sample. The morphology and orientation relationships among various phases have been found. In-situ microscpy heating studies show that melt initially spreads along the matrix–particle interface leading to a core-shell microstructure. And in the core of the core-sell particles, first Bi phase melts later Pb_7Bi_3 phase will melt and during cooling the whole particle solidify as biphase particle with large undercooling. In-situ heating studies carried out to study the size dependent melting and solidification behavior of biphase particles. During heating smaller particles melt melt first later bigger particle will melt. In contrast, while cooling smaller particles solidifies first, later bigger particles will solidify. Detailed high temperature x-ray diffraction studies indicate there increases first Bi phase peaks disappear later Pb_7Bi_3 phase peaks disappear and during cooling first Pb_7Bi_3 phase peaks appear and later Bi phase peaks appear.

In alloy2[Zn-2at%(Pb_{70}-Bi_{30})] inclusions were found to be single phase particles. X-ray diffraction study shows the presence of hcp Pb_7Bi_3 and hcp Zn phases in Zn-2at%(Pb_{70}-Bi_{30}) melt spun sample. The crystallographic orientation relationship between hcp Pb_7Bi_3 and hcp Zn phases. In-situ microscpy heating studies show that melting initiates across the matrix–particle interface grows gradually into the interior of the particle. Three phase equilibrium at peritectic reaction temperature is not observed during insitu heating TEM studies. Size dependent melting point depression of single phase particles is not observed from in-situ heating studies. Detailed high temperature x-ray diffraction studies show that while heating the Pb_7Bi_3 phase peak intensities start decreasing after 170°C and become zero at 234°C. And during cooling Pb_7Bi_3 phase peaks starts appearing at 200°C and on further cooling the Pb_7Bi_3 phase peak intensities increase upto 150°C, below this temperature peak intensities remain constant.